

Rayleigh-Schrödinger Perturbation Theory Scheme along the Pauli contribution

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ABSTRACT

A new Rayleigh-Schrödinger perturbation theory (RSPT) scheme along the Pauli (P) contribution is presented, with the unpertubated system being the artificial Kohn-Sham (KS) system of noninteracting fermions, which is linked to the real system of interacting fermions via the Hohenberg-Kohn theorem, with $\beta = 0$, i.e. no Pauli contribution, is scaled up by the coupling strength $0 \leq \beta \leq 1$ to a fictitious system, with $\beta = 1$, i.e. full Pauli contribution, the pertubated system of noninteracting bosons given by the Levy-Perdew-Sahni (LPS) equation. This formalism is introduced in order to give a pathway for constructing novel Kinetic energy density functionals (KEDF) for the Pauli kinetic energy as an (generalized) adiabatic-connection-like (GAC) theorem similar as to for constructing KS correlation functionals with the adiabatic-connection fluctuation-dissipation (ACFD) theorem or as been done in Görling-Levy perturbation theory (GLPT).

I. INTRODUCTION: THE ADIABATIC CONNECTION FLUCTUATION-DISSIPATION (ACFD) THEOREM FOR THE KOHN-SHAM (KS) CORRELATION ENERGY

We start at the adiabatic-connection fluctuation-dissipation (ACFD) theorem for the KS correlation energy [9], [10], [11], [12]

$$E_C^{ACFD}[\rho] = -\frac{1}{2\pi} \int_0^1 d\alpha \int_0^\infty d\omega \int dr dr' f_H(r, r') [\chi_\alpha(i\omega, r, r') - \chi_0(i\omega, r, r')] \quad (1)$$

Which equals

$$E_C[\rho] = E[\rho] - E_S[\rho] = \langle \Psi | \hat{H} | \Psi \rangle - \langle \Phi_S | \hat{H} | \Phi_S \rangle = T_C[\rho] + V_C[\rho] \quad (2)$$

Where $T_C[\rho] = \langle \Psi | \hat{T} | \Psi \rangle - \langle \Phi_S | \hat{T} | \Phi_S \rangle$ is the kinetic part and $V_C[\rho] = \langle \Psi | \hat{V}_{ee} | \Psi \rangle - \langle \Phi_S | \hat{V}_{ee} | \Phi_S \rangle$ the interaction part of correlation. By considering the perturbative adiabatic-connection (AC) Schrödinger equation, where the electron-electron interaction $\hat{V}_{ee} = \sum_{i<j} r_{ij}^{-1}$ is scaled by the coupling strength $0 \leq \alpha \leq 1$ and for $\alpha = 1$ $\hat{v}(\alpha = 1) = v(r)$ turns into the external potential and $\Psi(\alpha = 1) = \Psi_0$ as $E(\alpha = 1) = E[\rho]$ is the exact groundstate wavefunction and energy, therefore the pertubated Schrödinger equation describing the real system of interacting fermions is the electronic Schrödinger equation, and for $\alpha = 0$ $\hat{v}(\alpha = 0) = v_S(r) = v(r) + v_{HXC}(r)$ turns into the KS potential (with the Hartree-Exchange-Correlation potential) and $\Psi(\alpha = 0) = \Phi_S$ turns in to the KS determinant and the KS energy $E(\alpha = 0) = E_S[\rho]$, thus the unpertubated Schrödinger equation is the many-body KS equation describing a system of noninteracting fermions, the artificial KS system

$$[\hat{T} + \hat{v}(\alpha) + \alpha \hat{V}_{ee}] \Psi(\alpha) = E(\alpha) \Psi(\alpha) \quad (3)$$

By invoking the fundamental theorem of calculus (FTC) and the Hellmann-Feynman theorem [13] one obtains the adiabatic-connection (AC) theorem for the KS correlation energy [11], [5], [6], [7], [8], [14]

$$\begin{aligned} E_C^{AC}[\rho] &= E_C(\alpha = 1) - E_C(\alpha = 0) \stackrel{FTC}{\iff} \int_0^1 d\alpha \frac{dE_C(\alpha)}{d\alpha} \stackrel{Hellmann-Feynman}{\iff} \int_0^1 d\alpha V_C(\alpha) \\ &= \int_0^1 d\alpha \frac{1}{2} \int dr dr' f_H(r, r') \rho_C(r, r', \alpha) \end{aligned} \quad (4)$$

Where $E_C(\alpha = 0) = 0$ and $\rho_C(r, r', \alpha) = -\frac{1}{\pi} \int_0^\infty d\omega [\chi_\alpha(i\omega, r, r') - \chi_0(i\omega, r, r')] = 2[\rho_2(r, r', \alpha) - \rho_2(r, r', 0)]$ is the correlation pair density .

II. RAYLEIGH-SCHRÖDINGER PERTUBATION THEORY (RSPT) ALONG THE PAULI (P) CONTRIBUTION AND A GENERALIZED ADIABATIC-CONNECTION-LIKE (GAC) THEOREM FOR THE PAULI KINETIC ENERGY DENSITY FUNCTIONAL (KEDF)

Looking at the Pauli (P) kinetic energy density functional (KEDF) consisting of the KS KEDF $T_S[\rho] = \langle \Phi_S | \hat{T} | \Phi_S \rangle \stackrel{SCr}{\iff} \sum_{i=1}^N \int dr \phi_i(r) \left(-\frac{1}{2}\Delta\right) \phi_i(r) \stackrel{PI}{\iff} \frac{1}{2} \sum_{i=1}^N \int dr |\nabla \phi_i(r)|^2$ and the von Weizsäcker KEDF [$T_W[\rho] = \int \frac{1}{8} \frac{|\nabla \rho(r)|^2}{\rho(r)} dr \stackrel{PI}{\iff} \int dr \sqrt{\rho(r)} \left(-\frac{1}{2}\Delta\right) \sqrt{\rho(r)} = \sum_{i=1}^N \frac{1}{N} \int dr \sqrt{\rho(r_i)} \left(-\frac{1}{2}\Delta\right) \sqrt{\rho(r_i)} = \sum_{i=1}^N \int dr \phi_B(r_i) \left(-\frac{1}{2}\Delta\right) \phi_B(r_i) \stackrel{SCr}{\iff} \langle \Phi_B | \hat{T} | \Phi_B \rangle = T_B[\rho]$ [19], [20] which links the KS system to the fictitious system of noninteracting bosons (whereas comparable the correlation energy links the KS system to the real system of interacting fermions)

$$T_P[\rho] = T_S[\rho] - T_W[\rho] = T(\beta = 0) - T(\beta = 1) \stackrel{FTC}{\iff} \int_1^0 d\beta \frac{dT(\beta)}{d\beta} = T_P^{GAC}[\rho] \quad (5)$$

One might try to construct a similar (generalized) adiabatic-connection-like (GAC) theorem.

Considering the Schrödinger equation of the unpertubated system, that being the KS system of noninteracting fermions with the coupling constant $\beta = 0$ with the KS equation [1], [2]

$$\left(-\frac{1}{2}\Delta(r) + v_S(r)\right) \phi_S(r) = \varepsilon_i \phi_S(r) \quad (6)$$

And the Schrödinger equation of pertubated system, that being the fictitious system of noninteracting bosons with the coupling constant $\beta = 1$ with the Levy-Perdew-Sahni (LPS) equation of Orbital-free density functional theory (OFDFT) / bosonic Schrödinger equation [3], [4], [20]

$$\left(-\frac{1}{2}\Delta + v_S(r) + v_P(r)\right) \sqrt{\rho(r)} = \mu \sqrt{\rho(r)} \quad (7)$$

Where the boson orbital corresponds to $\phi_B(r) = \frac{1}{\sqrt{N}} \sqrt{\rho(r)}$. We invoke a Rayleigh-Schrödinger perturbation theory (RSPT) sheme [17], [18] along the Pauli (P) contribution $v_P(r) = \frac{\delta T_P[\rho]}{\delta \rho(r)} = \frac{\delta T_S[\rho]}{\delta \rho(r)} -$

$v_W(r, [\rho])$ with the coupling constant $0 \leq \beta \leq 1$, where $v_W(r, [\rho]) = \frac{\delta T_W[\rho]}{\delta \rho(r)} = \frac{1}{8} \frac{|\nabla \rho(r)|^2}{\rho^2(r)} -$

$\frac{\Delta \rho(r)}{4\rho(r)} \stackrel{PI}{\iff} \frac{(-\frac{1}{2}\Delta)\sqrt{\rho(r)}}{\sqrt{\rho(r)}}$ is the von Weizsäcker potential, we arrive at the following novel perturbative Schrödinger equation

$$\left(-\frac{1}{2}\Delta + v_S(r) + \beta v_P(r)\right) \phi_i(\beta, r) = \varepsilon_i(\beta) \phi_i(\beta, r) \quad (8)$$

We can look a bit closer at the GAC theorem for the Pauli kinetic energy and with the product rule, the Hermicity of the KE operator and its invariance to β as well as Slater-Condon rules (SCr) yields

$$T_P^{GAC}[q] = \int_1^0 d\beta \frac{d}{d\beta} \sum_{i=1}^N \left\langle \phi_i(\beta, r) \left| -\frac{1}{2} \Delta \right| \phi_i(\beta, r) \right\rangle = 2 \int_1^0 d\beta \sum_{i=1}^N \left\langle \frac{d\phi_i(\beta, r)}{d\beta} \left| -\frac{1}{2} \Delta \right| \phi_i(\beta, r) \right\rangle \quad (9)$$

Notice here, that the Hellmann-Feynman theorem [13] cannot be applied, since the β -dependent KE $T(\beta) = \sum_{i=1}^N \left\langle \phi_i(\beta, r) \left| -\frac{1}{2} \Delta \right| \phi_i(\beta, r) \right\rangle$ is no eigenvalue to the perturbative Schrödinger equation, but the FTC can indeed be utilized. Integration by parts (PI) gives the Pauli KEDF back

$$T_P[q] = 2 \sum_{i=1}^N \left\langle \phi_i(\beta, r) \left| -\frac{1}{2} \Delta \right| \phi_i(\beta, r) \right\rangle \Big|_{\beta=1}^{\beta=0} - 2 \int_1^0 d\beta \sum_{i=1}^N \left\langle \phi_i(\beta, r) \left| -\frac{1}{2} \Delta \right| \frac{d\phi_i(\beta, r)}{d\beta} \right\rangle \quad (10)$$

We acknowledge for the Slater Condon rules (SCr), that the many-body wave function of the KS system is a KS (Slater) determinant

$$\Phi_S(r_1, r_2, \dots, r_N) = \det(\{\phi_S(r_i)\}) \quad (11)$$

And the many-body wavefunction of the noninteracting boson system is in the simplest case a Hartree product (or a more sophisticated permanent $\Phi_B(r_1, r_2, \dots, r_N) = \text{perm}(\{\phi_B(r_i)\})$ respectively)

$$\Phi_B(r_1, r_2, \dots, r_N) = \prod_{i=1}^N \phi_B(r_i) \quad (12)$$

We also make the constraint, that the density stays invariant with respect to the coupling constant, similar to the regular adiabatic-connection (AC) $\forall \alpha \in [0, 1] : \varrho(r) = \langle \Psi(\alpha) | \hat{\varrho}(r) | \Psi(\alpha) \rangle$ as

$$\forall \beta \in [0, 1] : \varrho(r) = \langle \Phi(\beta) | \hat{\varrho}(r) | \Phi(\beta) \rangle \quad (13)$$

If we assume, that we can express $\phi_i(\beta, r)$ in a Maclaurin series, that converges

$$\phi_i(\beta, r) = \sum_{j=0}^{\infty} \beta^j \phi_i^{(j)} = \phi_i^{(0)} + \beta \phi_i^{(1)} + \beta^2 \phi_i^{(2)} + \dots \quad (14)$$

Where the 0-st order contribution is the KS orbital $\phi_i^{(0)} = \phi_S(r)$. We can find for the derivative

$$\frac{d\phi_i(\beta, r)}{d\beta} = \sum_{j=0}^{\infty} j \beta^{j-1} \phi_i^{(j)} = \phi_i^{(1)} + 2\beta \phi_i^{(2)} + 3\beta^2 \phi_i^{(3)} + \dots \quad (15)$$

We can construct the 1-st order contribution in terms of KS orbitals ϕ_S as

$$\phi_i^{(1)} = \sum_{t \neq i} \phi_t \frac{\langle \phi_t | v_P(r) | \phi_i \rangle}{\varepsilon_i - \varepsilon_t} \quad (16)$$

We can analogously construct higher order contributions and see that for $\beta = 1$

$$\begin{aligned} \phi_B(r) = \phi_i(\beta, r)|_{\beta=1} &= \frac{1}{\sqrt{N}} \sqrt{\varrho(r)} = \sum_{j=0}^{\infty} \phi_i^{(j)} = \phi_i^{(0)} + \phi_i^{(1)} + \phi_i^{(2)} + \dots \\ &= \phi_S(r) + \sum_{j=1}^{\infty} \phi_i^{(j)} \end{aligned} \quad (17)$$

Looking at the orbital energy in a power series

$$\varepsilon_i(\beta) = \sum_{j=0}^{\infty} \beta^j \varepsilon_i^{(j)} = \varepsilon_i^{(0)} + \beta \varepsilon_i^{(1)} + \beta^2 \varepsilon_i^{(2)} + \dots \quad (18)$$

Where the 0-st order contribution is just the KS orbital energy $\varepsilon_i^{(0)} = \varepsilon_i$ and the 1-st order contribution

$$\varepsilon_i^{(1)} = \langle \phi_i | v_P(r) | \phi_i \rangle = \left\langle \phi_i \left| \frac{d\hat{h}(\beta)}{d\beta} \right| \phi_i \right\rangle = \left. \frac{d\varepsilon_i(\beta)}{d\beta} \right|_{\beta=0} \quad (19)$$

Corresponds to applying the Hellmann-Feynman theorem [13] to the coupling-constant-dependent orbital energy evaluated at $\beta = 0$. The 2-nd order contribution is therefore

$$\varepsilon_i^{(2)} = \sum_{\substack{t \\ t \neq i}} \frac{\langle \phi_t | v_P(r) | \phi_i \rangle \langle \phi_i | v_P(r) | \phi_t \rangle}{\varepsilon_i - \varepsilon_t} \quad (20)$$

We can arrive at the Euler-Lagrange equation of DFT as

$$\begin{aligned} \varepsilon_i(\beta)|_{\beta=1} &= \sum_{j=0}^{\infty} \varepsilon_i^{(j)} = \varepsilon_i^{(0)} + \varepsilon_i^{(1)} + \varepsilon_i^{(2)} + \dots = \varepsilon_i + \sum_{j=1}^{\infty} \varepsilon_i^{(j)} = \mu = \frac{\delta E[\rho]}{\delta \rho(r)} \\ &= \frac{\delta T_S[\rho]}{\delta \rho(r)} + v_S(r) = v_W(r) + v_S(r) + v_P(r) = v_W(r) + v_B(r) \end{aligned} \quad (21)$$

III. THE BARTOLOTTI-ACHARYA (BA) AND LEVY-OU YANG (LO) FORMULAS FOR THE EXACT PAULI POTENTIAL

We shall lastly note, that the Pauli potential is known exactly in terms of KS orbitals from the Bartolotti-Acharya (BA) [15] or Levy-Ou Yang (LO) formulas [16] as

$$v_P(r) = \frac{\tau_S(r) - \tau_W(r)}{\rho(r)} + \sum_{i=1}^N (\mu - \varepsilon_i) \frac{|\phi_i(r)|^2}{\rho(r)} \quad (22)$$

Where $\tau_S(r) = \frac{1}{2} \sum_{i=1}^N |\nabla \phi_i(r)|^2$ is the KS KED, $\tau_W(r) = \frac{1}{8} \frac{|\nabla \rho(r)|^2}{\rho(r)}$ the von Weizsäcker KED and lastly $\tau_P(r) = \frac{1}{2\rho(r)} \sum_{i < k} |\phi_i(r) \nabla \phi_k(r) - \nabla \phi_k(r) \phi_i(r)|^2$ the Pauli KED. Thus we can write the respective KEDF

$$T[\rho] = \int dr \tau(r) \quad (23)$$

IV. COMPARISON OF KOHN-SHAM DENSITY FUNCTIONAL THEORY (KSDFT) TO ORBITAL-FREE DENSITY FUNCTIONAL THEORY (OFDFT)

We can write the in principal exact energy density functional in a suitable way for KSDFT [1], [2] and OFDFT [4] respectively

$$\begin{aligned} E[\rho] &= F_{HK}[\rho] + \int dr v(r) \rho(r) = T_S[\rho] + \int dr v(r) \rho(r) + E_{Hxc}[\rho] \\ &= T_W[\rho] + \int dr v(r) \rho(r) + E_{Hxc}[\rho] + T_P[\rho] \end{aligned} \quad (24)$$

Where $E_H[\rho] = \frac{1}{2} \iint dr dr' f_H(r, r') \rho(r) \rho(r')$ is the Hartree energy, $v_H(r) = \frac{\delta E_H[\rho]}{\delta \rho(r)} = \int dr' \rho(r') f_H(r, r')$ the Hartree potential and $F_{HK}[\rho]$ the Hohenberg-Kohn functional [1] and in OFDFT for approximating the exchange-(correlation) functional and potential mostly the Local density approximation (LDA) is used from Dirac [23] or Slater exchange $E_X[\rho] = -C_X \int dr \rho^{\frac{4}{3}}(r) \Leftrightarrow v_X(r, [\rho]) = \frac{\delta E_X[\rho]}{\delta \rho(r)} = C_X \frac{4}{3} \rho^{\frac{1}{3}}(r)$ with $C_X = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{\frac{1}{3}}$, whereas in KSDFT the exchange energy is evaluated with KS orbitals, which can be done exactly in an Exact Exchange (EXX) method and the correlation energy for e.g. with the ACFD theorem in the Random Phase Approximation (RPA). Note that in regular OFDFT the Pauli KEDF is being approximated as

$$T_P[\rho] = T_{TF}[\rho] + T_W[\rho, \nabla \rho, \Delta \rho] + T_{NL}[\rho](r, r') \quad (25)$$

Where $T_{TF}[\rho] = C_{TF} \int dr \rho^{\frac{5}{3}}(r)$ with $v_{TF}(r, [\rho]) = \frac{\delta T_{TF}[\rho]}{\delta \rho(r)} = C_{TF} \frac{5}{3} \rho^{\frac{2}{3}}(r)$ is the Thomas-Fermi (TF)

KEDF [21], [22] with its respective TF potential and the TF constant $C_{TF} = \frac{3(3\pi^2)^{2/3}}{10}$ and $T_{NL}[\rho]$ is a

nonlocal KEDF correction. The von-Weizsäcker functional can be interpreted as Generalized Gradient Approximation (GGA) or meta-GGA.

V. GÖRLING-LEVY PERTUBATION THEORY (GLPT)

With coupling-strength α -dependent Görling-Levy perturbation theory (GLPT) [5], [6]

$$E[\varrho] = T_S[\varrho] + E_{HX}[\varrho] + E_C = E_0 + E_1 + \sum_{j=2}^{\infty} E_j \quad (26)$$

Where $E(\alpha) = \sum_{j=0}^{\infty} \alpha^j E_j$ we see that the 1st order contribution is the Hartree-Exchange term and all higher orders $j \geq 2$ correspond to the correlation energy. The correlation energy in GLPT is different from the expression we give for the Pauli KEDF in a GAC theorem.

VI. OUTLOOK

It would be groundbreaking, if the GAC theorem could be in the future brought into an ACFD-like form as

$$T_P^{GACFD}[\varrho] \stackrel{?}{\Leftrightarrow} C \int_1^0 d\beta \int_0^{\infty} d\omega \iint dr dr' f_P(r, r', \omega) [\chi_S(i\omega, r, r') - \chi_B(i\omega, r, r')] \quad (27)$$

Because that would mean, that the exact Kinetic energy $T[\varrho] = \langle \Psi | \hat{T} | \Psi \rangle$ could be calculated as a sole functional of density, if we consider in Time-dependent orbital-free density functional theory (TDOFDFT) in the linear response (LR) regime with the Pauli kernel $f_P(r, r', \omega) = \frac{\delta v_P[\varrho](r, \omega)}{\delta \varrho(r', \omega)}$, which might in the simplest case be approximated with the TF kernel $f_{TF}(r, r') = \frac{\delta v_{TF}[\varrho](r)}{\delta \varrho(r')} = \frac{10}{9} \delta(r - r') \varrho^{-\frac{1}{3}}(r)$ or the more complicated vW kernel $f_W(r, r') = \frac{\delta v_W[\varrho](r)}{\delta \varrho(r')}$, the following Dyson equation [20]

$$\chi_S(i\omega, r, r') = \chi_B(i\omega, r, r') + \iint dr'' dr'''' \chi_B(i\omega, r, r'') \beta f_P(r, r'', \omega) \chi_S(i\omega, r'', r') \quad (28)$$

For linking the KS Response function $\chi_S(i\omega, r, r') = \frac{\delta \varrho[v_S](r, \omega)}{\delta v_S(r', \omega)}$ to the bosonic response function $\chi_B(i\omega, r, r') = \frac{\delta \varrho[v_B](r, \omega)}{\delta v_B(r', \omega)} = \frac{\delta \varrho[v_W](r, \omega)}{\delta v_W(r', \omega)}$. This stays in contrast to higher order gradient-expansions of the density [3]

$$T[\varrho] = T_{TF}[\varrho] + T_W[\varrho, \nabla \varrho, \Delta \varrho] + C_2 \int dr \varrho^{\frac{1}{3}}(r) \left[\left(\frac{\Delta \varrho(r)}{\varrho(r)} \right)^2 - \frac{9}{8} \left(\frac{\Delta \varrho(r)}{\varrho(r)} \right) \left(\frac{\Delta \varrho(r)}{\varrho(r)} \right)^2 + \frac{1}{3} \left(\frac{\nabla \varrho(r)}{\varrho(r)} \right)^4 \right] + \dots \quad (29)$$

- [1] P. Hohenberg and W. Kohn. Inhomogeneous Electron Gas. *Phys. Rev. B* 136, 864 (1964)
- [2] W. Kohn and L. J. Sham. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev. A* 140, 1133 (1965)
- [3] M. Levy, J. P. Perdew and V. Sahni. Exact differential equation for the density and ionization energy of a many-particle system. *Phys. Rev. A* 30, 2745 (1984)
- [4] J. Lehtomäki et al. Orbital-free density functional theory implementation with the projector augmented-wave method. *J. Chem Phys.* 141, 234102 (2014)
- [5] A. Görling and M. Levy. Correlation-energy functional and its high-density limit obtained from a coupling-constant perturbation expansion. *Phys. Rev. B* 47, 13105 (1993)
- [6] A. Görling and M. Levy. Exact Kohn-Sham scheme based on perturbation theory. *Phys. Rev. A* 50, 196 (1994)
- [7] A. Görling and M. Levy. Hardness of molecules and the band gap of solids within Kohn-Sham formalism: A perturbation-scaling approach. *Phys. Rev. A* 52, 4493 (1995)
- [8] A. Görling. Density-functional theory beyond the Hohenberg-Kohn theorem. *Phys. Rev. A* 59, 3359 (1999)
- [9] D. C. Langreth and J. P. Perdew. The exchange-correlation energy of a metallic surface. *Solid State Commun.* 17, 1425 (1975)
- [10] D. C. Langreth and J. P. Perdew. The exchange-correlation energy of a metallic surface: Wave-vector analysis. *Phys. Rev.* 15, 2884 (1977)
- [11] A. Heßelmann and A. Görling. Random-Phase approximation correlation methods for molecules and solids. *Mol. Phys.* 109, 2473 (2011)
- [12] A. Görling. Hierarchies of methods towards the exact Kohn-Sham correlation energy based on the adiabatic-connection fluctuation-dissipation theorem. *Phys. Rev. B* 99, 235120 (2019)
- [13] R. P. Feynman. Forces in Molecules. *Phys. Rev.* 56, 340 (1939)
- [14] A. Görling and M. Levy. Ionization Formulas and a DFT Perturbation Theory for Exchange and Correlation, Through Adiabatic Connection. *Int. J. Q. C.* 29, 93 (1995)
- [15] L. J. Bartolotti and P. K. Acharya. On the functional derivative of the kinetic energy density functional. *J. Chem. Phys* 77, 4576 (1982)
- [16] M. Levy and H. Ou-Yang. Exact properties of the Pauli potential for the square root of the electron density and the kinetic energy functional. *Phys. Rev. A* 38, 625 (1988)
- [17] E. Schrödinger. Quantisierung als Eigenwertproblem. *Annalen der Physik* 80, 437 (1926)
- [18] J. W. S. Rayleigh. *Theory of sound*. Vol. 1 (2nd ed.) p.115, London (1894)
- [19] C. F. von Weizsäcker. Zur Theorie der Kernmassen. *Zeitschrift für Physik* 96, 431 (1935)
- [20] K. Jiang and M. Pavanello. Time-dependent orbital-free density functional theory: Background and Pauli kernel approximation. *Phys. Rev. B* 103, 245102 (2021)
- [21] L. H. Thomas. The Calculation of Atomic Fields. *Math. Cambridge Philos. Soc.* 23, 542 (1927)
- [22] E. Fermi. Un Metodo Statistico per la Determinazione di alcune Proprietà dell'Atomo. *Accad. Lincei* 6, 602 (1927)
- [23] P. A. M Dirac. Note on Exchange Phenomena in the Thomas Atom. *Proc. Cambridge Philos. Soc.* 26, 376 (1930)